# BP SPILL

## QUALITY ASSURANCE SAMPLING PLAN TO EVALUATE THE EFFECTS TO AIR, WATER AND SEDIMENT FROM OIL AND DISPERSANT TO SHORE-LINE, NEARSHORE AND FAR OFF-SHORE AREAS

**EPA REGIONS 4/6**

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# EXECUTIVE SUMMARY

The U.S. Environmental Protection Agency (EPA) plans to conduct water, sediment and air sampling, analysis and monitoring to examine the effects of the BP Spill along the Gulf Coast, including off the coast of Louisiana, Mississippi, Alabama, and Florida. Additional portions of the Gulf Coast (e.g., Texas) may be added if the extent of the oil spill expands. Although impacts are closest to U.S. waters, the Agency also recognizes the potential impacts on international waters and the waters of other countries. Because of the potentially long-term nature of the response to the BP Spill, the government is concerned that the crude oil, dispersant application, and response technologies may have negative short- and/or long-term impacts on the aquatic environment as the spill moves to and within the near-shore environment. In order to monitor the spill, EPA has developed this Quality Assurance Sampling Plan (QASP) to assess the chemical contamination and toxicity to water and air as a result of the BP Spill.

## METHODLOGY OVERVIEW

EPA will conduct water, sediment and air sampling and monitoring from far off-shore, near-shore, and shoreline positions relative to the Gulf shoreline. This sampling approach is designed to provide EPA with feedback on the effects of dispersant application. Sampling includes the following approach:

- Visual monitoring relies on visual observations by trained observers. Following surface application of dispersant, trained observers will determine the extent to which dispersion has occurred.

- Fluorescence monitoring combines the visual monitoring with real-time water column monitoring utilizing a submersible fluorometer that is towed by boat at specified depths within the plume and outside the plume. Water samples may also be taken for later analysis at a laboratory.

- Laboratory sampling and analyses will be instituted as a baseline in the event that fluorometer monitoring indicates the approach of the plume. This effort includes the collection of water samples from within the dispersed oil plume and outside the plume for spectrofluorometric analysis and laboratory analyses of parent and alkyl polycyclic hydrocarbons (PAHs) and benzene, toluene, ethylbenzene, and xylene (BTEX) constituents. Samples analyses also includes chemical oxygen demand (COD), biological demand (BOD), dissolved oxygen (DO), and ecotoxicity analyses to include acute and short-term chronic testing of standard toxicity test species indicative to the Gulf.

EPA will also conduct air sampling to assess the potential impacts to air quality and possible exposure as a result of oil dispersant application. Air sampling has been designed to quantify volatile components of the dispersants currently being used in the spill response. Measurements for volatile organic compounds will be conducted via two EPA methods which were selected due to their applicability on board a marine vessel and the ability to acquire a short-term grab sample with detection limits low enough to meet ambient air data quality objectives.

## SUMMARY OF ONGOING ACTIVITIES

EPA has been conducting air sampling of particulate matter (PM2.5) as well as volatile organic chemicals (VOCs) at air sampling locations along the Gulf Coast. Air sampling equipment include BGI PQ200 air samplers, used to collect air samples for PM2.5 and SUMMA® canisters with a 12-hour flow controller collecting ambient air for VOC analysis. Tedlar bags are being utilized to collect grab samples for VOC analysis as necessary.

Additionally, air monitoring activities include the use of DataRAM DR-4000 instrumentation to monitor the particulate levels, AreaRAE PGM-5020 to collect readings for VOCs and MultiRAE instrumentation to monitor for H2S and CO. EPA has also utilized the TAGA Mobile Laboratory that provides mobile monitoring for the selected compounds of interest (i.e., benzene, toluene, ethylbenzene, and xylenes).

EPA has also been assessing water and sediment quality along the Gulf Coast. Multiple project teams have been deployed to multiple locations collecting surface water and sediment samples and collecting real-time water data utilizing multi-parameter water quality instruments. Additional sampling, to determine the presence of free oil globules and/or surface oil at near shore surface water locations (i.e., within 100 feet of the shoreline), was conducted to characterize the oil and dispersant mixture that is reaching the shoreline. Further sampling along beaches, marshes, tidal flats, or other shoreline types was conducted to collect samples of fresh oil, mousse, tar, tarballs, tar patties that had accumulated as part of the oil release. Samples are being analyzed for VOCs, semivolatile organic chemicals (SVOCs), metals (including mercury), total petroleum hydrocarbon (TPH), oil and grease, toxicity in sediments, and total organic carbon.

Additional water and sediment samples will be collected during the National Coastal Condition Assessment (NCCA) which is scheduled to be initiated in June 2010. The NCCA data will be used to supplement the planned post-impact water and sediment sampling.

# 1. INTRODUCTION

The U.S. Environmental Protection Agency (EPA) plans to conduct water, sediment, and air sampling analysis and monitoring to examine the effects of the BP Spill along the Gulf Coast, including off the coast of Louisiana, Mississippi, Alabama, Florida. Additional portions of the Gulf Coast (e.g., Texas) may be added if the extent of the oil spill expands. Although impacts are closest to U.S. waters, the Agency also recognizes the potential impacts on international waters and the waters of other countries. Proposed monitoring locations are shown in Figures 3-1 and 3-2, which are focused at this time on areas from the Louisiana/Texas boundary to the Florida panhandle. Expansion to coastal areas of Texas and the west coast of Florida will occur as needed and in anticipation to spill migration. This Quality Assurance Sampling Plan (QASP) was prepared EPA Regions 6 and 4 in coordination with headquarters personnel including the multiple offices, regional water quality divisions, regional air programs, and Environmental Response Team (ERT) personnel. This plan describes the technical scope of work to be completed as part of this Emergency Response.

EPA is concerned with the potential impact of dispersant chemicals and crude oil on public health and on shore-line and near shore aquatic environments. Because of the potentially long-term nature of the spill impacts and the ongoing response, a robust study of the public health and environmental impacts of the spill and response is needed.

## 1.1 PROJECT OBJECTIVES

The objective of this sampling plan is to provide assessment of the chemical contamination and the toxicity to water, sediment and air resulting from the spill and response. The plan provides for sampling from three general positions relative to the Gulf shoreline: shoreline, nearshore and far off-shore sampling. Sampling will be conducted for chemical constituents of dispersant compounds and crude oil. In addition, samples will also be collected at all locations for ecotoxicity assessments. The plan provides for air sampling at the nearshore and far off-shore locations.

Shoreline air sampling from multiple platforms is already being conducted as part of the emergency response (Appendices D and E). Additionally, surface water and sediment sampling activities are also being performed (Appendices F). Planned surface water and sediment shoreline

sampling is included in Appendix G. These activities are complimented by air and water sampling, analysis, and monitoring activities that normally occur under state and federal programs in Gulf States.

This document summarizes the methods that will be used for the sampling, analysis, and monitoring. The frequency of these activities and maps of their likely locations are provided.

## 1.2 PROJECT TEAM

The Project Team will consist of the necessary EPA and EPA contractor personnel to implement the monitoring and sampling strategies described herein. The project team will consist of a site lead(s) and the necessary number of operational person to implement the approach included herein. In addition, EPA and EPA contractor personnel will be assigned as necessary to facilitate successful implementation.

EPA and potentially ERT members will also be on-site to assist with coordination and on-site direction of sampling, data collection, and analysis as needed. EPA will coordinate with the Unified Command as necessary.

# 2. SITE DESCRIPTION AND BACKGROUND

The BP Spill source is located approximately 52 miles southeast of Venice, Plaquemines Parish, Louisiana, (28.73667˚ N, -88.38722˚ W). The source is a leaking production well caused by damage from the sinking of the Transocean Deepwater Horizon drill rig at BP Site Mississippi Canyon 252. The size of the impacted area resulting from the release varies from day-to-day, but is presently several hundred square miles in size. The spill is affected by wind and wave action, which continues to impact the size, shape, and movement of the oil. The potential impact zone includes the shorelines of Louisiana, Mississippi, Alabama, Florida and Texas.

# 3. SAMPLING APPROACH AND PROCEDURES

The sampling approach that will be applied to the BP Spill is discussed in this section. In general, the sampling plan consists of the following activities:

- Water and Sediment Sampling Analysis and Monitoring
  - Shoreline Water and Sediment Sampling
  - Nearshore Water Sampling
  - Far Off-shore Water Sampling
- Air Sampling, Analysis and Monitoring
  - Shoreline (ongoing; Appendix D and E)
  - Nearshore
  - Far Off-shore
- On-going Sediment and Surface Water Sampling (Appendix F)

Sampling methods, locations, quality assurance (QA) procedures, and the analytical approach and methods that will be used are discussed in the following sections. This plan may be increased or modified as necessary to address areas beyond those identified herein.

## 3.1 OVERVIEW OF SAMPLING ACTIVITIES

EPA will conduct sampling, analysis and monitoring as outlined herein.

### 3.1.1 Data Quality Objectives

Data Quality Objectives (DQOs) have been developed using the seven-step process set out in the *EPA Guidance for Quality Assurance Project Plans:* EPA QA/G-5. The shoreline, near-shore and off-shore water and air DQOs established for this project are included in Appendix A.

### 3.1.2 Health and Safety Implementation

Maintaining and assuring the health and safety of all EPA personnel is the top priority of this sampling effort. EPA will provide planning functions consistent with activities and responsibilities of the Incident Command System (ICS). At the beginning of each operational period, a daily operation meeting will be held post to discuss objectives of the operational period, division assignments, field instrumentation calibration and use, and health and safety protocol.

EPA sampling activities will be conducted in accordance with the site-specific Health and Safety Plan (HASP). EPA will conduct the sampling activities in Level D personal protective equipment (PPE), with the potential to upgrade PPE as necessary, and as stated in the site HASP. The Field Team Leader (FTL) or designated Field Safety Office (FSO) will be responsible for implementation of the HASP during the sampling activities.

EPA personnel will be instructed to communicate unsafe situations immediately to supervisors and co-workers, and to immediately take appropriate measures. Sampling activities will be stopped whenever necessary to assure the safety of all engaged personnel.

## 3.2 WATER SAMPLING

Water sampling activities will be conducted in accordance with the EPA guidelines, standard industry practices; and with EPA ERT and Regional Standard Operating Procedures (SOPs). The site-specific sampling activities are described in the following subsections. For reference, SOPs supporting this QASP are included in Appendix B. Water samples will be collected at shorelines, nearshore (3-mile limit) and far off-shore at distances between 3 and 50 miles.

### 3.2.1 Offshore Sampling

EPA and EPA contractor personnel will conduct far off-shore sampling/monitoring activities, which are designed to provide EPA with feedback on the effects of dispersant application.

Monitoring relies on visual observation by a trained observer. Following surface application of dispersant, the observers shall determine by visual observation the extent to which dispersion has occurred. The observers must score the appearance of the dispersed oil plume on a scale of 1 to 5, with 5 being the highest level of dispersion visually observed and 1 being no dispersion at all. These observations shall be made at several times after the dispersant application (immediately after application, 30 minutes later, and 60 minutes later). Additional monitoring combines the visual monitoring with real-time water column monitoring. These measurements shall be made continuously for a period of 1 hour after dispersant application.

Field observations, including digital photographs, shall be collected to assist the EPA in documenting the data for future use. The field team shall record the time, instrument readings, and

relevant observations at selected time intervals. Global positioning system (GPS) instruments will be used to ascertain the exact position of each reading.

#### *3.2.1.1 Far Off-shore Dispersant Area Assessment Locations*

Since dispersant application area locations are currently unknown, sample locations will be determined by the locations of dispersant applications utilizing visual monitoring and real-time water column monitoring. Following dispersant application, transects shall be run parallel to the direction of the predominant wind throughout the dispersant-application area. Transects shall be positioned at regular intervals to characterize the extent of the dispersant application area. Transects will be initiated 100 m beyond the visual oil plume and will extend through the dispersant application area and 100 m into the untreated oil plume (if present). A submersible spectrofluorometer shall be towed by boat through the treated area as described at specified depths. Fluorometric measurements shall be made continuously for a period of 1 hour after dispersant application. Grab samples will be collected along transects at approximately 200-m intervals consistent with the aforementioned approach. Upon EPA direction, samples for laboratory analyses will be collected at locations based on field observations. Field parameters include pH, conductivity, dissolved oxygen (DO), and turbidity. DO measurements may be taken using Method 360.1 (via membrane probe) or via Method 360.2 (Winkler method).

Prior to arriving at a sample station, reference fluorescence values using a submersible spectrofluorometer or onboard field fluorometer shall be determined. For each sample location (or transect), EPA contractor personnel will deploy the submersible spectrofluorometer or collect water samples for onboard or subsequent laboratory-based fluorometric analysis using the field spectrofluorometer, or equivalent laboratory-based analytical equipment.

### 3.2.2 Shoreline and Nearshore Assessment

Nearshore water sampling activities involve fluorometry, chemical, and ecotoxicity analysis. As described above, visual observation of a plume in open waters is expected. In the nearshore area, fluorescence and laboratory analyses will predominate. Because of the critical nature of this plan as an early warning system, it is desirable to have as rapid a turnaround of quality-assured results as possible. For this reason, an expedient turnaround time should be requested for all laboratory analyses. Specific laboratory information is discussed in Section 4 of this QASP.

The submersible spectrofluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm) shall be towed by boat at the sampling location specified in Section 3.2.2.1. If it is determined that submersible and onboard spectrofluorometer analyses cannot be properly conducted, then samples shall be preserved with 0.02 mL of 10% hydrochloric acid (HCl) and brought to shore to be analyzed at a fixed laboratory where a scanning spectrofluorometer is set up. Care should be taken to avoid contaminating the sampler with standing oil or surface sheen. These samples will provide quantitative information on the approach of the dispersed plume, and the information may be used by National Oceanic and Atmospheric Administration (NOAA) to refine its trajectory modeling. Reconnoitering sorties may be made periodically between the 3 mile limit and the nearest edge of the spill until the spectrofluorometer gets a reading above the reference value.

Additional biological and chemical laboratory analyses will be instituted as a baseline, in the event that fluorometer monitoring indicates the approach of the plume. Samples shall be taken within the dispersed oil plume, if present, and approximately 100 m outside the plume (for reference values). These samples shall be split and preserved following methods described above.

#### *3.2.2.1 Shoreline Monitoring Sample Locations*

The shoreline monitoring locations will return to the same locations that were sampled to characterize the initial conditions at the beginning of the response (Appendix F – EPA Region 6 Water and Sediment QASP and Appendix G – EPA Region 4 Beach and Sediment QASP). If visible oil is observed or detected, a sediment sample must be collected and analyzed using the procedures specified in the above mentioned QASPs.

#### *3.2.2.2 Nearshore Monitoring Sample Locations*

Sampling locations for fluorometer measurements and laboratory analyses were pre-determined using Visual Sampling Program (VSP) software. VSP is a software tool that supports the development of a defensible sampling plan based on statistical sampling theory and the statistical analysis of sample results to support confident decision making. VSP randomly identified the location of the sample stations using a one-sample proportion test for 95% confidence level. A total of 70 sample stations are located along the 3 mile limit: 35 are located within EPA Region 4 and 35 are located within EPA Region 6. Information regarding station identification and geo-

graphic position (latitude, longitude in decimal degrees) in included in Appendix C. Water quality samples for chemistry and toxicity testing will be collected at each location.

Prior to arriving at a sample station, reference fluorescence values will be determined using the submersible spectrofluorometer or onboard field spectrofluorometer. For each sample location, the following sampling/survey procedure shall be followed:

1. Deploy the submersible spectrofluorometer or collect water samples for onboard fluorometric analysis using the field spectrofluorometer (see Subsection 3.2.4).

2. Collect water samples for laboratory chemistry and biological analyses (see Subsection 3.2.5.2).

3. Evaluate the percent difference between the reference values and station values. If the station values are greater than 20% of the reference value, it is likely that polycyclic aromatic hydrocarbons (PAHs) from dispersed oil are present. If present, then transit to a location outside of the dispersed plume, and collect a reference water samples for laboratory chemistry and biological analyses (see Subsection 3.2.5.2).

4. Return to the planned target sampling station and initiate surveys of fluorescence by deploying the fluorometer. Continue along the 3-mile limit for a distance of approximately three kilometers or the next sampling station, whichever comes first (see Subsection 3.2.4).

### 3.2.3 Vessels of Opportunity and Navigation

Water quality surveys and sampling will be conducted from vessels of opportunity. As such, there are no specific requirements for each vessel other than each vessel must be: (1) operated by a U.S. Coast Guard (USCG)-licensed captain (consideration should be given to captains with local knowledge of water conditions); (2) provisioned with properly maintained safety equipment; and (3) equipped with GPS instruments capable of continuously recording vessel position. The vessel's GPS should be capable of receiving differential corrections from the USCG or Wide Area Augmentation System (WAAS) corrections from the Federal Aviation Administration (FAA). Each vessel should have adequate deck space for the safe deployment, retrieval and operation of water samplers, as well as for storage of water samples as determined by the Health and Safety Officer.

### 3.2.4 Continuous In Situ Fluorescence Measurements

If it is determined that fluorescence is required, continuous measurements of in situ fluorescence will be conducted. Although measurements of fluorescence do not provide specific concentrations of PAHs in the water column, they will give a qualitative assessment of fluorescence relative to reference readings in order to determine the location of the dispersed oil plume. A spectrofluorometer (excitation wavelength of 320 nm and emission wavelength of 400-600 nm), or equivalent, shall be towed by boat at 1-m and 2-m depths in order to collect simultaneous measurements of fluorescence at increasingly deeper depths. The units shall be secured to a load bearing weighted tow line in order to maintain near vertical assessments of the water column while under way. Deployment and operation of the fluorometers will be conducted in accordance with the standard operating procedures provided by the manufacturer.

### 3.2.5 Water Sample Collection

Water samples shall be collected to satisfy fluorescence monitoring or laboratory objectives. For fluorescence monitoring, water samples may be collected at each station if *in situ* measurements of fluorescence are not practicable due to sea conditions or other logistical or environmental constraints. Water samples collected for fluorescence monitoring shall be analyzed for fluorescence using an onboard field spectrofluorometer(s) operating at excitation wavelengths of 280 nm, 340 nm and 445 nm, and calibrated to the manufacturers' operating procedure. If it is determined that onboard spectrofluorometer analyses cannot be properly conducted, then samples shall be preserved with 0.02 mL of 10% hydrochloric acid (HCl) and brought to shore to be analyzed at a fixed laboratory where a scanning spectrofluorometer is set up. For laboratory analyses, waters samples shall be collected at each station for chemical and ecotoxicity (i.e., bioassay) analyses.

#### *3.2.5.1 Water Samples for Fluorescence Monitoring*

Fluorescence monitoring water samples shall be collected only if *in situ* measurements of fluorescence are not collected. Two samples from each station shall be collected. One sample shall be collected at 1 m depth; the second sample shall be collected at 2 m depth.

Samples shall be collected into the cuvette provided with the field fluoremeter or equivalent. Operation of the field fluoremeter shall be conducted according to the standard operating procedure provided by the manufacturer.

#### *3.2.5.2 Laboratory Samples*

Two samples from each station shall be collected. One sample shall be collected at 2 m depth; the second sample shall be collected at 10 m depth. Two triplicate samples shall be collected at each location.

Water samples for laboratory analyses shall be collected utilizing the same methods employed for fluorescence analyses. Water samples shall be collected for dissolved and total metals. Water samples shall be filtered and preserved while in the field. A 0.45 μm filter capsule filter or equivalent must be used to filter the dissolved metal samples. The capsule filter can be connected to a sample-delivery system (e.g., peristaltic pump) that generates sufficient pressure (positive or negative) to force water through the filter.

Solar radiation monitoring of spectral wavelength and intensity shall be conducted at each station with a radiometer when water samples are collected for laboratory analyses. These data will be used to ground truth the ecotoxicity tests under photoenhanced conditions. Radiometer measurements shall be collected to measure the attenuation of ultraviolet (UV) light in water. The radiometer shall measure the UVA range between 320 nm to 400 nm which corresponds to the range of light that can photoenhance PAH toxicity. A submersible radiometer shall be towed to measure UV light at a depth of approximately 2 m for continuous measurement. The radiometer shall be used to measure UV light while the vessel is stationary at initial target depths of 0.5, 1.0, 1.7, 3.0, 5.5 and 10 m to measure light attenuation. Field notes shall be recorded to document the weather conditions (e.g., presents of clouds and haze). Stationary measurements shall be taken at the location of the nearshore water sample.

## 3.3 FAR OFF-SHORE AND NEARSHORE AIR SAMPLING

In order to assess the potential impacts to air quality and possible exposure as a result of oil dispersant application, this air sampling scheme has been designed to quantify volatile components of the dispersants currently being used in the spill response. Two dispersants formulations are currently being used to respond to the BP Spill. Both dispersants contain propylene glycol and a propriety organic sulfonic acid salt. These two materials are common emulsifying components, have minimal human toxicity, have very low vapor pressure, and can only exist in the air phase as droplets or mist. In addition to these materials the dispersants contain organic solvents. In the

case of first dispersant the solvent is a light petroleum distillate (CAS 64742-47-8) similar to common kerosene. For the second dispersant, the solvent is 2-butoxyethanol, a common industrial solvent. Since sampling will occur on board sampling vessels in off-shore and near-shore operation, a simple straightforward sampling approach is desirable. The methodology is consistent with the on-shore sampling programs currently underway (see Appendix D and E).

EPA Methods TO-15 and TO-17 were selected due to their applicability on board a marine vessel and the ability to acquire a short term grab sample with detection limits low enough to meet ambient air data quality objectives. Samples shall be collected upwind of the sampling vessel engine exhaust and any other obvious sources of non-dispersant or spill related volatile organic chemicals (VOCs).

EPA Method TO-17 can provide results for semi-volatile and aerosolized hydrocarbons that may exhibit poor recovery from SUMMA canisters using EPA Method TO-15. Appropriate sorbent tubes are available for the light petroleum distillates, propylene glycol, and 2-butoxyethanol. Laboratory experience indicates a 1-liter sample at 100 mL/min can achieve detection limits of about 200 parts per billion (ppb) for the petroleum distillates, 160 ppb for the propylene glycol and 10 ppb for the 2-butoxyethanol.

## 3.4 ONGOING AIR SAMPLING AND MONITORING

Due to the BP Spill, EPA has been conducting air sampling of particulate matter (PM2.5) as well as VOCs at air sampling locations along the Gulf Coast. Air sampling equipment include BGI PQ200 air samplers, used to collect air samples for PM2.5 and SUMMA® canisters with a 8-hour and 24-hour flow controller collecting ambient air for VOC analysis, and TO-17 equipment for dispersant compound analysis. Tedlar bags are being utilized to collect grab samples for VOC analysis as necessary. 24-hour SVOC samples are also being collected using PUF high volume samplers and PUF/XAD cartridges per EPA Compendium method TO-13.

Additionally, air monitoring activities are ongoing and include DataRAM DR-4000 instrumentation to monitor the particulate levels, AreaRAE PGM-5020 to collect readings for VOCs using a 10.6 electron volt (eV) photoionization detector (PID) lamp, and MultiRAE instrumentation are being utilized to monitor for H2S and CO using chemical specific electrochemical sensors. EPA has also utilized the TAGA Mobile Laboratory that provides mobile monitoring for the selected

compounds of interest (i.e., benzene, toluene, ethylbenzene and xylenes). ERT/SERAS also provide quick turnaround analysis of selected compounds for samples collected in Tedlar bags.

Details regarding protocols and procedures for on-going air sampling and monitoring are included as Appendices D and E.

## 3.5 ONGOING AND PLANNED WATER AND SEDIMENT SAMPLING

As a result of the BP Spill, EPA has been assessing water and sediment quality along the Gulf Coast. Multiple project teams have been deployed to multiple locations based upon site conditions and operations. As the meteorological and operational situations change, sampling and monitoring teams and operations have adapted, based upon direction from the Unified Command. EPA has been collecting surface water and sediment samples and collecting real-time water data utilizing multi-parameter water quality instruments. Additional sampling, to determine the presence of free oil globules and/or surface oil at near shore surface water locations (i.e., within 100 feet of the shoreline), is being conducted to characterize the oil and dispersant mixture that is reaching the shoreline. Further sampling along beaches, marshes, tidal flats, or other shoreline types is being conducted to collect samples of fresh oil, mousse, tar, tarballs, tar patties that had accumulated as part of the oil release. Samples are being analyzed for VOCs, semi-volatile organic chemicals (SVOCs), metals (including mercury), total petroleum hydrocarbon (TPH) for gas range organics (GRO), diesel range organics (DRO) and oil range organics (ORO), oil and grease, toxicity in sediments, and total organic carbon. Field parameters include the collection of pH, conductivity, dissolved oxygen (DO) and turbidity.

Additional water and sediment samples will be collected during the National Coastal Condition Assessment (NCCA) which is scheduled to be initiated in June 2010 and is planned to be collected as part of the post-impact sampling that will return to locations sampled during the initial part of the response.

Details regarding protocols and procedures for on-going and planned surface water and sediment sampling are included as Appendices F and G, respectively.

### 3.5.1 Quality Assurance/Quality Control Samples

EPA contractor personnel shall collect blind field duplicate/triplicate samples of water and equipment rinsate blanks during the sampling effort. Quality assurance/quality control (QA/QC) samples shall be collected according to *Guidance for Quality Assurance Project Plans*, US EPA QA/G-5.

The EPA and EPA contractor personnel will be responsible for QA/QC of the field investigation activities. Laboratories utilized during the field activities will be responsible for QA/QC related to the analytical procedures including the analysis of MS/MSD spike duplicates. All data will be validated and approved by EPA.

## 3.6 SAMPLE MANAGEMENT

Sample handling, nomenclature and container/equipment decontamination procedures are discussed in the following subsections.

### 3.6.1 Sample Handling Procedures

Water samples will be collected using equipment and procedures appropriate to the matrix, parameters, and sampling objectives. The volume of the sample collected will be sufficient to perform the analysis requested. Samples will be stored in the proper types of containers and preserved in a manner for the analysis to be performed per laboratory guidelines. Personnel responsible for sampling will change gloves between each sample collection/handling activity.

The sample containers will be handled using gloves appropriate for the hazards involved with handling of petroleum spill related samples (e.g., nitrile). The gloves serve two purposes, (1) personnel protection, and (2) prevention of sample cross-contamination. The gloves shall be replaced at a minimum between each sample collected or as frequently as needed.

Air samples will be collected using equipment and procedures appropriate to TO-15 and TO-17 as applicable, and these sampling objectives. Short term TO-15 grab samples will be collected in SUMMA canisters over two to three minutes time using a laboratory supplied filter and vacuum gauge to monitor the sampling rate. Samples should be collected such that 2 to 3 inches of mercury vacuum remains after sample collection. Samples shall be collected upwind of the sam-

pling vessel engine exhaust and any other obvious sources of non-dispersant or spill related VOCs.

TO-17 samples shall be collected using laboratory supplied sampling tubes and SKC (or equivalent) low flow sampling pumps set to 100 mL/min flow rate for a period of 10 minutes. Sample flow rates shall be measured before and after each sample collection event using a BIOS DryCal or Buck Scientific primary standard flow calibrator. Samples shall be collected upwind of vessel exhaust and other obvious sources not related to the spill or dispersant application. Following collection, samples will be assembled and catalogued prior to shipping to the designated laboratory.

### 3.6.2 Sample Nomenclature

Sample identification involves the assignment of sample location numbers and sample depth indicators to all samples collected during the sampling activity. The EPA will specify the sample location number and depth of the samples in the field. Sampling personnel shall record this information using a permanent marker on a label applied to the side of the container.

For the purposes of the activity, each sample will receive an individual identification number consisting of a four-digit number (ex. SW01). This four-digit number will be followed by a two digit number which will be used to identify the sample depth as follows: 1 meter below surface (01), 10 meters below surface (10). A QC Code for the type of sample is added to designate a sample as normal (11), duplicate (12), or rinsate (43).

An example, Sample ID is: SW01-01-11. This number corresponds to a normal subsurface water sample collected at a depth of 1 meter below surface from location SW01.

Blind field duplicate samples will be identified in the same manner as the sample locations and will also follow in sequential order. These samples will be given a unique sample number so as not to be obvious to the laboratory.

### 3.6.3 Sample Container and Equipment Decontamination

Each sample shall be collected with clean decontaminated equipment. Equipment decontamination will be required to prevent contamination of clean areas and cross-contamination of samples

and to maintain the health and safety of field personnel. Decontamination of all sampling equipment will occur prior to sampling and between each sample location. Decontaminated sampling equipment and sample containers will be maintained in a clean, segregated area. Appropriate equipment decontamination procedures for field sampling equipment will be followed according to applicable EPA, ERT and EPA contractors' SOPs.

Equipment decontamination will be completed in the following steps:

- Tap water and Alconox Luminox® rinse with soft scrub brush
- Deionized water rinse, three times

Personnel decontamination procedures will be described in the site-specific HASP that will be prepared by EPA contractor personnel and reviewed by the EPA prior to implementation of activities at the site.

## 3.7 SAMPLE PRESERVATION AND HOLD TIMES

EPA and EPA contractor personnel will obtain and use precleaned sample containers for water samples collected during the sampling effort. Laboratory samples will be stored in coolers with ice until they are submitted for analysis.

Once collected, SUMMA canister air samples will be stored in their shipping boxes. TO-17 samples will be sealed and placed in individual storage vials supplied by the laboratory. TO-17 sorbant tube sample will be maintained at 4° C at all times after sample collection. The maximum holding time for TO-15 is 30 days from sample collection, and the maximum holding time for TO-17 is 28 days from sample collection. TO-17 sorbent tube samples and SUMMA canisters will be analyzed by a laboratory selected by the EPA.

EPA will request 24-hour turnaround time for water analytical results unless otherwise advised based on discussions with the laboratory. Turnaround time is initiated when the samples are received at the laboratory and continues until the analytical results are made available to EPA. EPA and EPA contractor personnel will also ensure that the maximum hold time, initiated when the samples are collected in the field, and continues until the samples are analyzed, are not exceeded. Samples that have been analyzed will be disposed by the designated laboratory in accordance with the laboratory SOPs.

# 4. ANALYTICAL AND LABORATORY APPROACH

Information regarding analytical methods and data validation procedures is discussed in the following sections.

## 4.1 ANALYTICAL METHODS

After samples are received by the laboratory, samples will be prepared and analyzed in accordance with the EPA SW-846 or appropriate methods. Laboratory turnaround time for samples is 24 hours from receipt of samples by the laboratory.

Deliverables will include preliminary data via email in PDF format and an Electronic Data Deliverable (EDD) in the Microsoft Excel format.

### 4.1.1 Chemistry Analytical Methods

Information regarding analytical methods, sample containers, preservation and hold times is included in Table 4-1. Appendix H contains the screening levels for water. EPA analytical capabilities may be supplemented by commercial laboratories.

Sorbent tube samples will be analyzed for TO-17 by Air Toxics Limited of Folsum, California. Hazardous Air Pollutants (HAPs) screening levels for TO-15 are included in Appendix I. EPA uses screening levels for an initial comparison of analytical data generated from a sample. Screening levels use conservative assumptions regarding exposure and toxicity, and are used as a tool to indicate whether or not further evaluation is warranted.

### 4.1.2 Ecotoxicity Methods

Ecotoxicity will be assessed using a two-phase approach: 1) rapid acute toxicity screening and (2) short-term chronic toxicity tests for those samples resulting in significantly reduced survival relative to control levels. Acute and short-term chronic toxicity tests shall be conducted concurrently. If acute toxicity is observed in the screening test, then the concurrent short-term chronic toxicity test shall be terminated for those samples. Each test shall have a control, and reference sample collected from non-impacted areas. A summary of information regarding analytical methods, sample containers, preservation and hold times is included in Table 4-1. The evaluation criteria for the ecotoxicity analyses are shown in the Figure 4-1.

## Table 4-1

## Analytical Methods, Container, Preservation and Holding Times
## BP Spill, Gulf Coast

| Name | Analytical Methods | Matrix | Container | Preservation | Minimum Volume or Weight | Maximum Holding Time |
|---|---|---|---|---|---|---|
| VOCs | SW846 8260B | Water | Glass (Tef-lon-lined septum for water) | 4°C, HCl to pH<2 | 4x40 ml vials | 14 days (7 days if un-preserved by acid |
| SVOCs | SW846 8270C | Water | Amber Glass, (Teflon- lined for water) | 4°C | 2 x 1 L | 7 days extract (water), 40 days analysis |
| Alkyl PAHs | ASTM D7363-07 or SW846 8272 | Water | Amber Glass, (Teflon- lined for water) | 4°C | To Be Determined | To Be Determined |
| TPH GRO | SW846 8015B | Water | Glass (Tef-lon-lined septum for water) | 4°C, HCl to pH<2 | 4x40 ml vials | 14 days (7 days if un-preserved by acid |
| TPH DRO and ORO | SW846 8015B | Water | Amber Glass, (Teflon- lined for water) | 4°C | 4x40 ml vials | 7 days extract (water), 40 days analysis |
| Metals (includ-ing mercury) (total and dissolved) | SW846 6010B and SW846 7470A | Water | Polyethylene | $HNO_3$ to pH<2 4°C | 500 ml | 28 days for mercury and 180 days all other metals |
| Dispersant indicator chemical | To Be Determined | Water | To Be Determined | To Be Determined | To Be Determined | To Be Determined |
| COD | Standard Me-thods 410.3 | Water | Glass | H2SO4, 4°C | 50 ml | 28 days |
| BOD | Standard Me-thod 5210 B (5-day BOD Test) | Water | Glass | 4°C | 1 L | 48 hours |
| DO, membrane probe[1] (or Winkler method) | EPA Method 360.1 (or 360.2) | Water | 1 x 250 ml HDPE Bottle[3] | 4°C | 300 ml | Analysis in 4 to 8 hrs[2] |
| VOCs | TO-17 | Air | Sorbant Tube | Reseal tube and cool to 4°C | 1 L @100 mL/min for 10 minutes | 28 days |

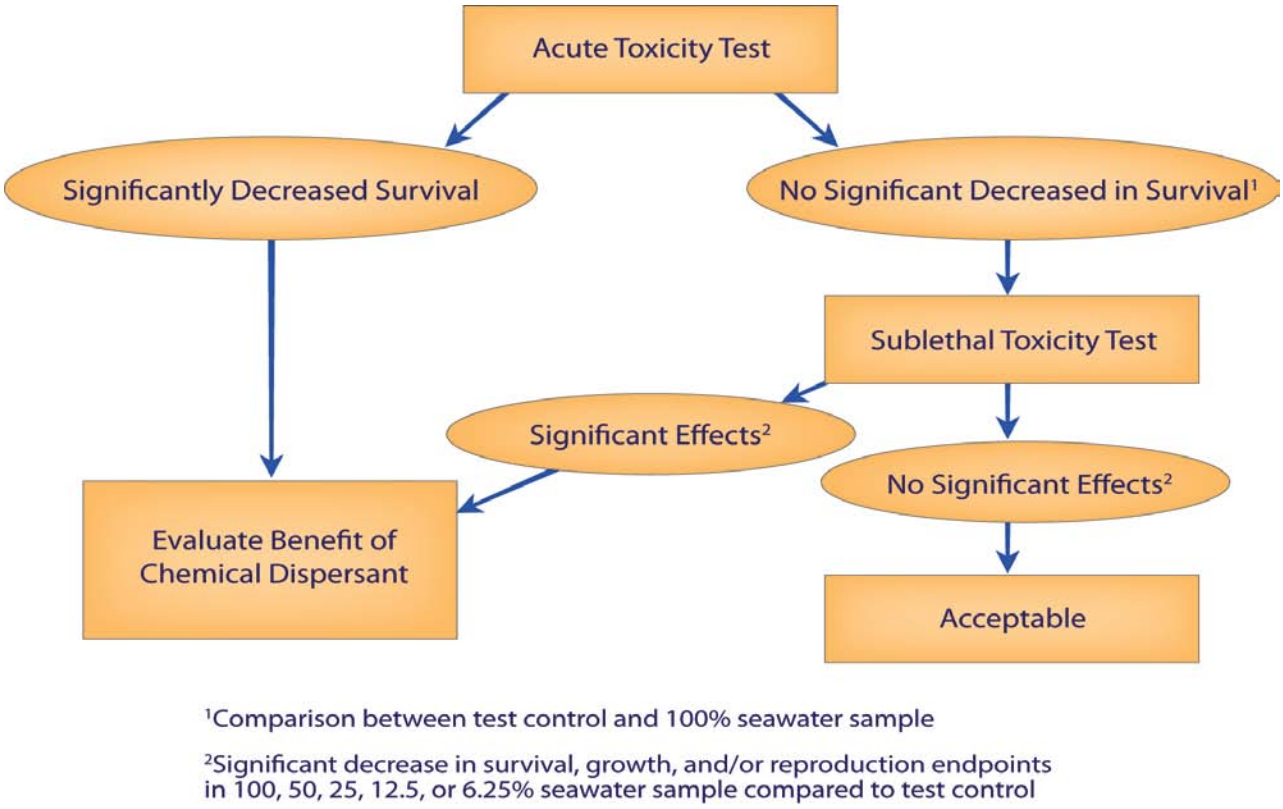
| Name | Analytical Methods | Matrix | Container | Preservation | Minimum Volume or Weight | Maximum Holding Time |
|---|---|---|---|---|---|---|
| VOCs | TO-15 | Air | SUMMA Canister | Maintain approximately 3" vacuum after collection | 6 liter @ 2L/min for 2-2.5 min grab sample collection | 30 days |
| *Americamysis bahia* Acute Toxicity Screen, Standard | EPA-821-R-02-012, Test Method 2007.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 1.5 L | 36 hours |
| *Menidia beryllina* Acute Toxicity Screen, Standard | EPA-821-R-02-012, Test Method 2006.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 3 L | 36 hours |
| *Americamysis bahia* Acute Toxicity Screen, Photo-enhanced | EPA-821-R-02-012, Test Method 2007.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 1.5 L | 36 hours |
| *Menidia beryllina* Acute Toxicity Screen, Photo-enhanced | EPA-821-R-02-012, Test Method 2006.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 2 3 L | 36 hours |
| *Americamysis bahia* Chronic Toxicity | EPA-821-R-02-014, Test Method 1007.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 16 L | 36 hours |
| *Menidia beryllina* Chronic Toxicity | EPA-821-R-02-014, Test Method 1006.0 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 16 L | 36 hours |
| *Arbacia punctulata* Chronic Toxicity | EPA/600/R-95/136 and ASTM E 1563 - 98 | Water | [1]Cubitainer, precleaned LDPE | Ice, ≤ 4°C, in dark environment | [2] 0.5 L | 36 hours |

[1]Preferred over glass containers for safety during shipment

[2]2-20L cubitainers + 1-5L cubitainer

**Figure 4-1**

**Toxicity Test**




#### *4.1.2.1 Acute Toxicity Screening Tests (Standard)*

Acute (96-hour) toxicity screening tests shall be performed to determine if 100% water samples cause mortality to aquatic organisms. Tests shall be performed on the inland silverside fish, *Menidia beryllina*, and the mysid shrimp, *Americamysis bahia*, in accordance with Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms (EPA, 2002). Each batch of test organisms shall be evaluated in reference toxicant tests and results shall be compared with historical control charts to establish test organism sensitivity.

#### *4.1.2.2 Acute Toxicity Screening Tests (Photo-Enhanced)*

Oil in the water column can be 10 times to greater than 100 times more toxic in the presence of natural sunlight. Photo-enhanced toxicity assessment will be used to assess the enhanced toxicity of simulated solar radiation using organisms exposed in the standard toxicity assays above.

Assessment of photo-enhanced toxicity is critical to a complete assessment of the potential impacts of the spill on aquatic life. Many waters of the Gulf are clear, allowing sunlight to penetrate and potentially enhance the toxicity of the oil. Photo-enhanced acute toxicity tests (i.e., conducted under full spectrum lights) will be performed concurrently with the standard acute screening tests (i.e., conducted under normal laboratory lighting) using the same test methods and batch of test organisms but in separate test facilities. Measurements of both light wavelength and intensity will be collected using a broad wavelength radiometer. The radiometer shall measure the UV range between 320 nm and 400 nm which corresponds to the range of the light than can photoenhance PAH toxicity. Light intensity will be measured by placing the detector at the bottom of surrogate test containers filled with reference water. Surrogate containers will be placed at multiple locations within the test facility and measurements will be made at both test initiation and termination. Similar measurements of wavelength and intensity will also be collected at select sampling locations in the field to facilitate the risk assessment (See Subsection 3.2.5.2).

#### *4.1.2.3 Short-term Chronic Toxicity Tests*

Short term chronic toxicity tests shall be conducted to provide an assessment of water column toxicity. Short-term chronic toxicity assays shall be performed on the inland silverside fish, *Menidia beryllina*, the mysid shrimp, *Americamysis bahia*, and the sea urchin, *Arbacia punctulata*. Test procedures shall be performed in accordance with Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Marine and Estuarine Organisms (EPA 2002), ASTM Method E 1563-98 (2004), and *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (EPA, 1995). Each batch of test organisms shall be evaluated in reference toxicant tests and results shall be compared with historical control charts to establish test organism sensitivity.

#### *4.1.2.4 Collection of Samples from Toxicity Tests for PAH Analysis*

For each toxicity test conducted, samples shall be collected from the 100% water sample at test initiation (1 sample for all tests initiated concurrently) and at test termination (1 sample from each test conducted) to detect any loss of oil constituents (e.g., adhesion to carboy) during shipment. Confirmatory chemical analyses shall include TPH, fluorometric analyses, SVOCs and alkyl-PAHs.

#### *4.1.2.5 Evaluation Criteria for Ecotoxicity Assessment*

If there are no significant differences in the ecotoxicity test results (survival, growth, and reproduction endpoints) between the control and the highest treatments (100% water sample), the evaluation will be a determination of acceptable risk to aquatic life. If toxicity is observed in 100% water sample or its dilutions, then EPA and NOAA will interpret the adverse results of the toxicity tests in conjunction with the benefits of dispersing the oil to inform ongoing determinations of utility of continued application of dispersants. Two repeated rounds of acceptable toxicity tests result (all endpoints) will elevate the biological monitoring to the EPA Regional Response Team (RRT) for potential discontinuation.

## 4.2 DATA VALIDATION

EPA will perform a Level 2 data validation on the analytical data generated by the laboratory using EPA-approved validation procedures in accordance with the EPA Contract Laboratory Program National Functional Guidelines for Organic and Inorganic Data Review. A summary of the data validation findings will be presented in Data Validation Summary Reports as part of the final report. EPA will evaluate the following applicable parameters to verify that the analytical data is within acceptable QA/QC tolerances.

# 5. QUALITY ASSURANCE

Quality assurance will be conducted in accordance with EPA protocols. EPA and EPA contractor personnel will be assigned and will monitor work conducted throughout the entire project including reviewing interim report deliverables and field audits. The EPA and EPA contractor personnel will be responsible for QA/QC of the field sampling and monitoring activities. The designated laboratory(s) utilized during the investigation will be responsible for QA/QC related to the analytical work. EPA and EPA contractor personnel will also collect samples to verify that laboratory(s) QA/QC is consistent with the required standards and to validate the laboratory data received.

## 5.1 SAMPLE CUSTODY PROCEDURES

### 5.1.1 Chain-of-Custody (COC)

This section describes the program requirements for sample handling and COC procedures. Samples are considered to be in custody if they are: (1) in the custodian's possession or view, (2) retained in a secured place (under lock) with restricted access, or (3) placed in a secured container. The principal documents used to identify samples and to document possession are COC records, field log books, and field tracking forms. COC procedures will be used for all samples throughout the collection, transport, and analytical process, and for all data and data documentation, whether in hard copy or electronic format. COC procedures will be initiated during sample collection and custody transfer.

Upon receipt at the laboratory, the laboratory receiving personnel will follow their standard login sampling procedures outlined in the laboratory's approved quality assurance program plan. The field team or courier will also be provided a receipt of sample login and a copy of the COC for their records.

### 5.1.2 Sample Shipment

The samples will be preserved and packaged in coolers with ice according to appropriate sample packing guidelines. In general, the samples will be shipped via overnight carrier to the partici-

pating laboratories by either the United Parcel Service (UPS) or Federal Express (Fed Ex). The Department of Transportation (DOT) and International Air Transport Association (IATA) regulations governing environmental and hazardous sample packaging, labeling and sampling will be followed.

EPA and EPA contractor personnel will prepare and complete chain-of-custody forms for all samples sent to an EPA designated off-site laboratory in accordance with standard COC procedures. Samples relinquished to the participating laboratories will be subject to standard COC procedures.

## 5.2 PROJECT DOCUMENTATION

Field observations and any changes to the sampling performed will be recorded legibly and in ink and by entry into field logbooks, Response Manager, or SCRIBE. EPA personnel will utilize SCRIBE for data entry on-site and will upload to the Response Manager Analytical module.

At the completion of the project, EPA will review and validate laboratory data and prepare a draft report of field activities and analytical results for EPA review. Draft deliverable documents will be uploaded to the EPA TeamLink® website for EPA review and comment.

# 6. REFERENCES

ASTM (American Society for Testing and Materials). 2009. E 1563-98 (Reapproved 2004) *Standard Guide for Conducting Static Acute Toxicity Tests with Echinoid Embryos*. In Annual Book of Standards, Vol. 11.06. West Conshohocken, PA.

EPA (U.S. Environmental Protection Agency). 2002. *Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms*. EPA-821-R-02-012. USEPA Office of Water. October.

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EPA (U.S. Environmental Protection Agency). 1995. *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms*. EPA/600/R-95/136. USEPA Office of Research and Development. August.

EPA (U.S. Environmental Protection Agency). 1999. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air – Second Edition.* EPA/625/R-96/010b.

EPA (U.S. Environmental Protection Agency). 2002. *Guidance for Quality Assurance Project Plans.* EPA/240/R-02/009.